(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number : **0 614 864 A1**

(12) EUROPEAN PATENT APPLICATION

(21) Application number : **94301541.2**

(22) Date of filing : **03.03.94**

(51) Int. Cl.^{5} : **C07C 1/04**

(30) Priority : **09.03.93 US 28444**

(43) Date of publication of application :
14.09.94 Bulletin 94/37

(84) Designated Contracting States :
BE DE FR GB IT NL

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(54) Heat removal in gas conversion process.

(57) A vaporizable cooling medium, suitably pentane, is used in a gas conversion process, for example a Fischer-Tropsch process, to consume and be vaporized by the exothermic heat of reaction. The thus vaporized medium may then be expanded to produce energy, for example to drive an air plant compressor to produce oxygen for use in the gas conversion process.

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This invention relates to the use of an inert, condensible medium, for removing heat from hydrocarbon synthesis reactions, for example a Fischer-Tropsch process.

Fischer-Tropsch processes invariably use water/steam as the cooling medium for this exothermic process. Thus, boiling water is pumped through cooling tubes in the reactor. As the reaction proceeds and heat is generated, it is absorbed by the water converting it to steam and thereby using the latent heat of vaporization to control reactor temperatures. Fischer-Tropsch reactions, particularly on a commercial scale, require many, many cooling tubes, whether for fixed bed or slurry operations, for maintaining proper temperatures. Thus, the risk of a tube failure or weld leak is compounded significantly. In the event of a tube leak, the contents of the reactor are normally at a higher pressure than a boiling water/steam coolant and reactor contents will leak into the cooling system resulting in severe contamination and ultimately shut down of the process. While steam/water cannot be pressurized to greater pressures than the reaction process, because the temperature would be too high, even if it could, a leak of steam into the process will tend to deactivate the Fischer-Tropsch catalyst.

In accordance with this invention, an inert, condensible medium, boiling at a pressure at or above, preferably above, the reaction pressure is employed as the cooling medium for Fischer-Tropsch reactions. (For purposes of this invention, inert means inert with respect to the relevant reaction, for example a Fischer-Tropsch reaction.) By using a material such as pentane, for example, which vaporizes at or above Fischer-Tropsch, or other, reaction pressures, cooling tube leaks will not lend to reactants or reaction products entering the cooling system. Rather, the pentane will leak out of the cooling tubes and into the reaction mixture where it will have no effect either on the cooling system or the Fischer-Tropsch process. In fact, n-pentane, for example, is a product of the Fischer-Tropsch process. Thus, the process makes hydrocarbons, such as C_6+ paraffins, and the process can thereby supply the cooling medium make up requirements.

In a preferred embodiment, the high pressure vaporized coolant is expanded through a turbo-expander, for example, or any piece of equipment that can take advantage of the work energy available. The energy thereby produced is recovered and utilized in the Fischer-Tropsch process, but is preferably used to operate compressors, particularly air plant compressors for separating oxygen from nitrogen so the oxygen can be used to generate synthesis gas for use in the Fischer-Tropsch process.

In the accompanying drawings, figure 1 shows a schematic arrangement for using pentane as the coolant for a Fischer-Tropsch process; and

Figure 2 shows a schematic for producing synthesis gas using an air plant.

The Fischer-Tropsch process is a well known process and operates at temperatures ranging from about 175-400°C, preferably about 190°C to about 275°C, and pressures of about 1 to 100 atmospheres, preferably about 10-40 atmospheres.

Essentially, the Fischer-Tropsch process converts synthesis gas, CO and hydrogen, in ratios ranging from about 1/1 to 4/1, preferably 1.5/1 to 2.5/1, to higher hydrocarbons, e.g., C_2+, preferably C_5+, over a Group VIII metal, preferably cobalt, supported catalyst. The cobalt may be promoted with a variety of materials, e.g., ruthenium, zirconium, rhenium, hafnium, titanium, etc. The catalyst support may vary widely and is usually selected from a group containing refractory metal oxides, e.g., silica, alumina, silica-alumina, titania, or zeolites.

The cooling medium must be inert, condensible, and at its boiling point is at a pressure greater than the reaction pressure. Suitable coolants are liquid paraffins (at room temperature) such as C_4 to C_{10} normal, iso and cyclic paraffins, olefins, substituted cyclic paraffins, e.g., methyl cyclohexane, low molecular weight silanes and silyl ethers, oxygenates silicone oils and their light analogs. Preferred materials are normal, iso, or cyclic paraffins, particularly C_4 to C_7 paraffins, particularly C_5-C_6 paraffins, e.g., n-pentane.

Turning now to Figure 1, reactor 10 may, for example, be operating at Fischer-Tropsch conditions of 15 atmospheres and 220°C. Liquid, high pressure pentane, e.g., about 25 atmospheres, stored in drum 14 is used to cool the reactor by flowing through line 13 into the reactor and through cooling tubes 12, absorbing the heat of reaction and vaporizing. The vapor is removed through line 15 and through the overhead of drum 14 at about 24 atmospheres (allowing for some pressure drop in the lines) and at about 190°C. The vaporized pentane is then sent by line 17 to expander 18 where the high pressure energy is recovered. The low pressure vapor leaving the expander, at about 105°C and 1.5 atmospheres, is fed by line 19 to condenser 20 where the pentane is liquefied, i.e., by cold water.or air, to about 50°C and then pumped up to pressure in pump or compressor 21 and then back through the storage drum 14 and the reactor 10 for another cycle.

In a preferred embodiment, at least a portion and preferably a substantial portion of the energy recovered from the expander is used to drive compressors for an air plant which separates oxygen from nitrogen. Additionally, the energy can be used to drive other compressors or turbogenerators which produce electricity to be used in the process, e.g., for driving compressors, pumps, etc. The oxygen recovered from the air plant is used, preferably in combination with steam and natural gas or other hydrocarbons, e.g., lower hydrocarbons, such as C_1-C_4 alkyls, and preferably the presence of a reforming catalyst, e.g., 1-10 wt% nickel on alumina, to produce CO and hydrogen, preferably in a fluid bed process operating at about 1600°C-2000°C and 15-40 atmospheres. The CO and hydrogen are subsequently reacted in reactor 10 to produce hydrocarbons comprising C_6+ liquids.

This preferred embodiment is illustrated in Figure 2 where the energy recovered from the expander is used to compress air entering the air plant 40 via line 41 where the compressed air is separated into nitrogen disposed of through line 44, and oxygen in line 45. The oxygen is fed to synthesis gas generator 50 where it is combined with natural gas, e.g., mostly methane, from line 47. Both the oxygen and the natural gas may be diluted with steam, lines 48 and 49. The synthesis gas is recovered from line 51 cooled in condenser 53 and forwarded to the Fischer-Tropsch reactor via line 54.

Essentially, operation of an air plant involves compressing and cooling air, first by water or ambient air, then by returning process streams (O_2, N_2 and "waste" mixtures of O_2 and N_2 as they are being warmed) and by reboiling the fractionation column, at which point the air is substantially condensed.

The air is then flashed into a tower, where it is fractionated and the products warmed against incoming air.

The use of non-corrosive hydrocarbons or silicone based fluids as cooling media eliminates the need for desalinization of water for a water/steam system. While a pentane system is not quite as efficient as a steam/water system, this is not a significant issue since excess steam is typically available in such systems; and the advantages of eliminating leak problems are manifest and, in the long run, the economics are more favorable.

Claims

1. A method for removing heat from a hydrocarbon synthesis process reaction zone, which comprises passing a cooling medium through the reaction zone, in indirect heat exchange therewith, thereby vaporizing the cooling medium; the cooling medium being inert, condensible, and vaporizing at a pressure which is at least as great as the pressure in the reaction zone.

2. The method of claim 1 wherein the reaction zone is at a temperature of from about 175°C-400°C and a pressure of from about 0.1 to 10.1 M Pa (1-100 atmospheres).

3. The method of claim 1 or claim 2, wherein the cooling medium is selected from C_4-C_{10} normal, iso, and cyclic paraffins, olefins, low molecular weight silanes, silyl ethers and silicone oils.

4. The method of claim 3 wherein the cooling medium is a C_4-C_7 normal, iso, or cyclic paraffin.

5. The method of claim 4 wherein the cooling medium is n-pentane.

6. The method of any preceding claim, wherein the high pressure, vaporized cooling medium is expanded thereby creating energy, and a substantial portion of the energy is recovered and used in the hydrocarbon synthesis process.

7. The method of any one of claims 1 to 5 wherein the high pressure vaporized cooling medium is expanded, thereby creating energy and a substantial portion of the energy is recovered and used for driving compressors in an air plant.

8. The method of claim 7 wherein the air plant separates oxygen from nitrogen and the oxygen is reacted with a lower hydrocarbon to produce hydrogen and CO.

9. The method of claim 8 wherein steam is present during the reaction of the oxygen and the hydrocarbon.

10. The method of claim 8 or claim 9, wherein the CO and hydrogen are reacted in the hydrocarbon synthesis process to produce C_2+ hydrocarbons.

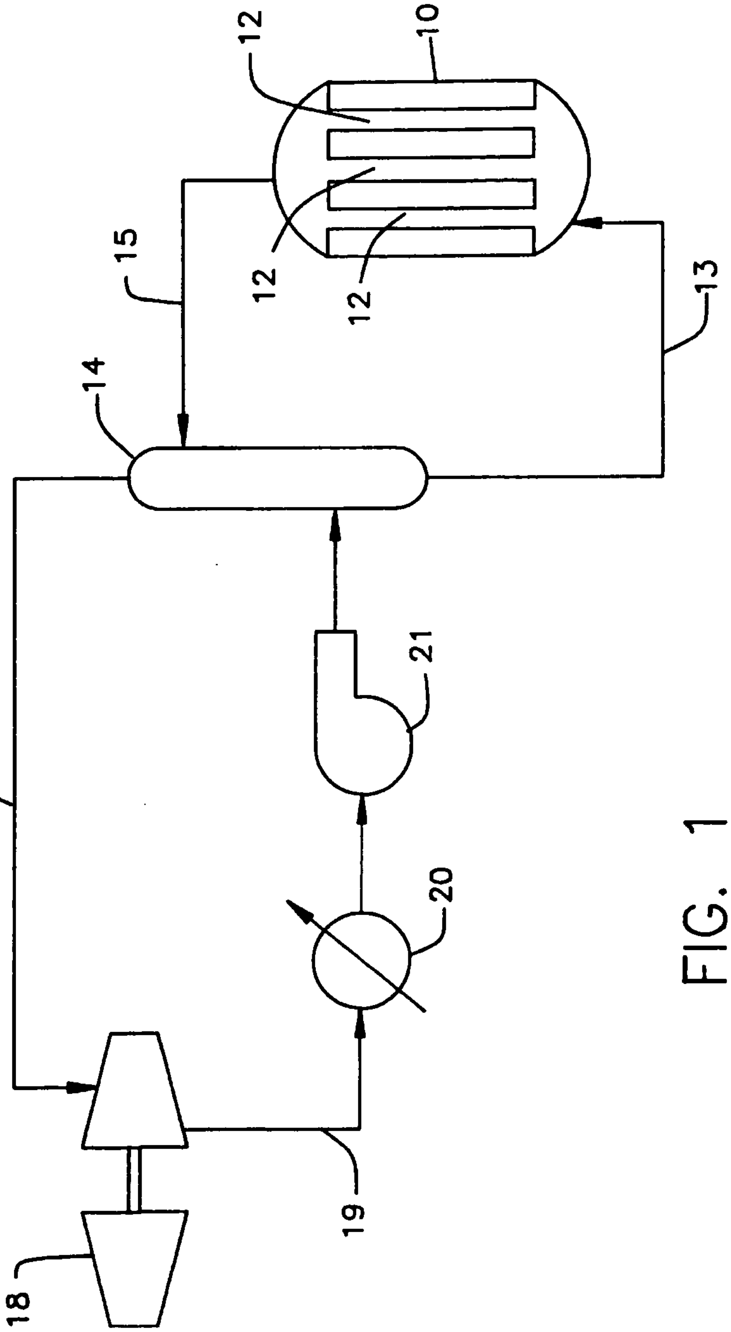

FIG. 1

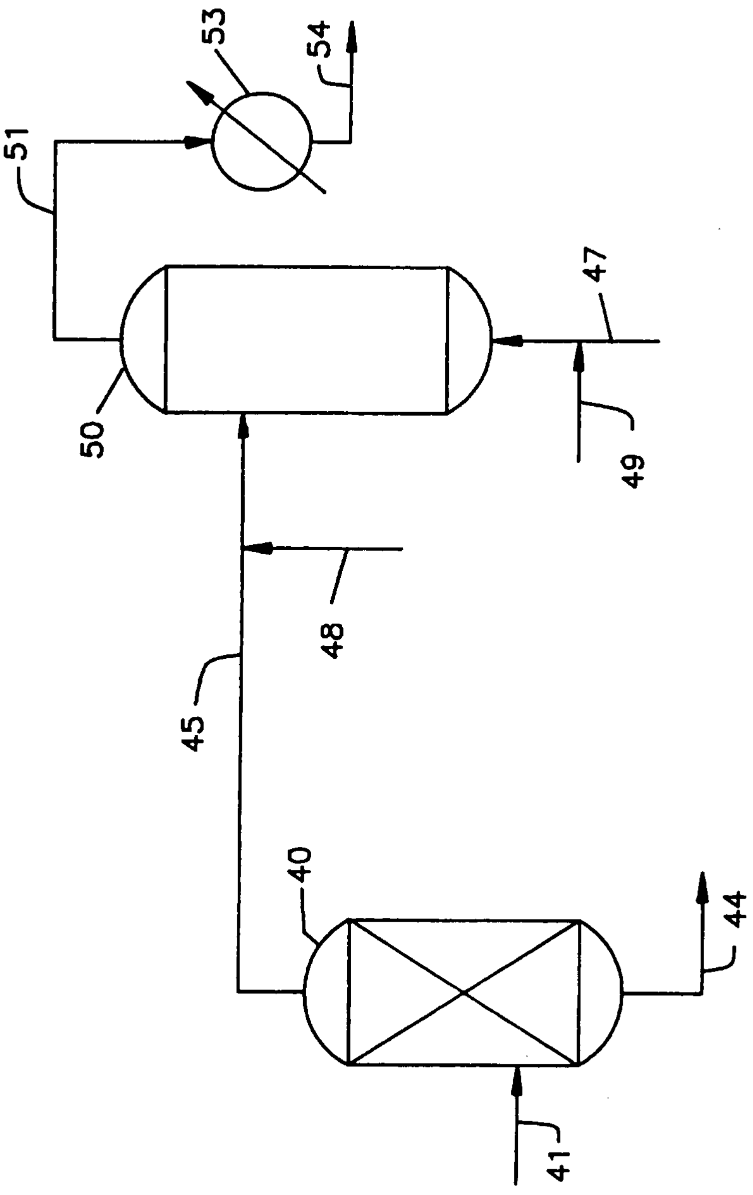

FIG. 2

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EUROPEAN SEARCH REPORT

Application Number
EP 94 30 1541

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
X	US-A-2 238 766 (L. ALBERTS) * page 1, right column, line 5 - line 32 *	1,2	C07C1/04
X	CH-A-275 423 (METALLGESELLSCHAFT) * example * * page 2, line 47 - line 56 *	1,3	
A	DE-A-28 34 589 (THYSSENGAS; DIDIER ENGINEERING) * page 6, paragraph 4 * * figure *	6	

TECHNICAL FIELDS SEARCHED (Int.Cl.5)

C07C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	11 May 1994	Van Geyt, J

CATEGORY OF CITED DOCUMENTS

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Y : particularly relevant if combined with another document of the same category
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